US006162762A

United States Patent [19]

Cornes et al.

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[45] **Date of Patent: Dec. 19, 2000**

[54] HERBICIDAL COMPOSITION

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[73] Assignee: **Novartis Crop Protection, Inc.**, Greensboro, N.C.

[21] Appl. No.: **09/235,348**

[22] Filed: **Jan. 21, 1999**

[30] **Foreign Application Priority Data**

Jan. 12, 1998 [CH] Switzerland 135/98

[51] **Int. Cl.**[7] **A01N 25/32**; A01N 43/653

[52] **U.S. Cl.** **504/105**; 504/106; 504/108; 504/112

[58] **Field of Search** 504/105, 106, 504/108, 112

[56] **References Cited**

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507171 10/1992 European Pat. Off. .

OTHER PUBLICATIONS

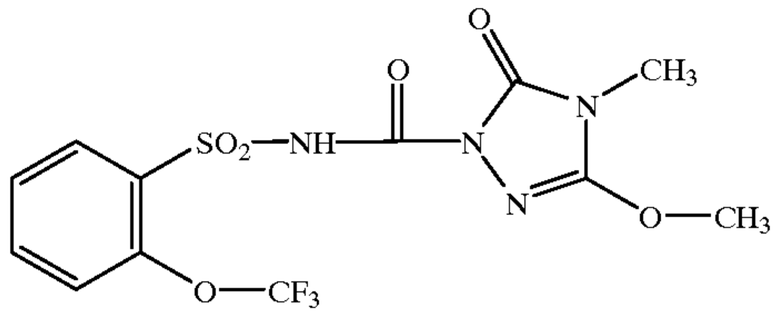
Devine et al. Physiology of Herbicide Action. Chapter 17.4: "Safeners for Herbicides". p.376–387, 1993.

Primary Examiner—S. Mark Clardy
Attorney, Agent, or Firm—William A. Teoli, Jr.

[57] ABSTRACT

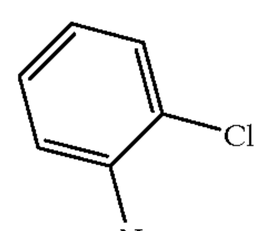
A selective herbicidal composition for controlling grasses and weeds in crops of cultivated plants, comprising a) a herbicidally effective amount of a herbicide of formula I

(I)

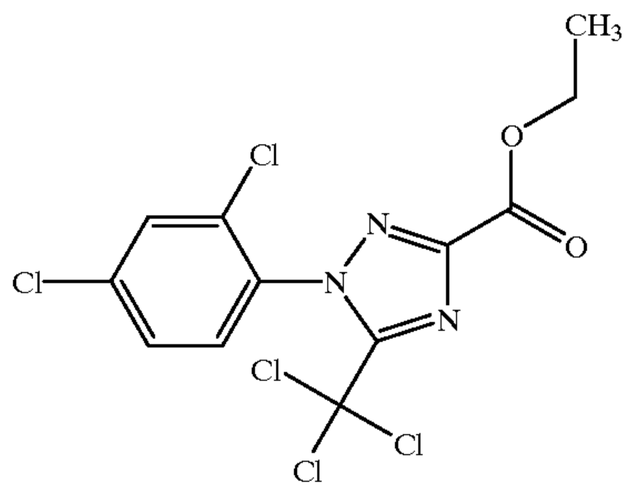


and b) to antagonise the herbicide, an antidotally effective amount of a safener selected from the group of the compounds of formula 1.01 (CGA 185,072), 2.01, 2.05, 3.03, 4.001, 5.006 (benoxacor), and 6.02 (fluxofenim).

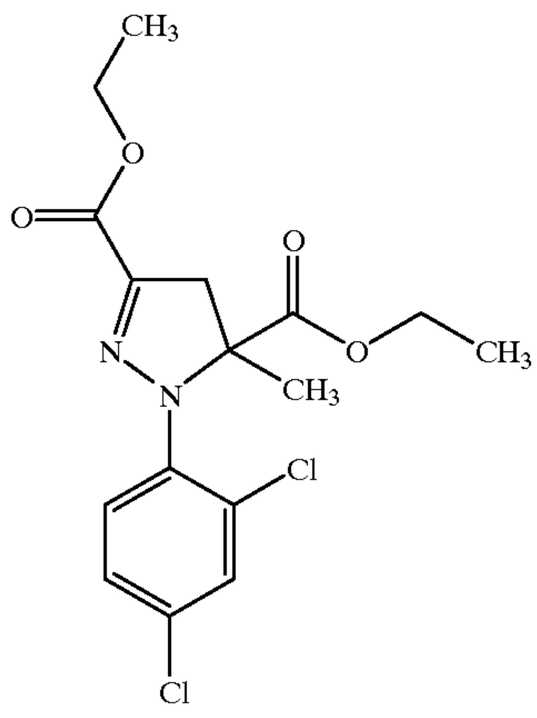
(2.01)



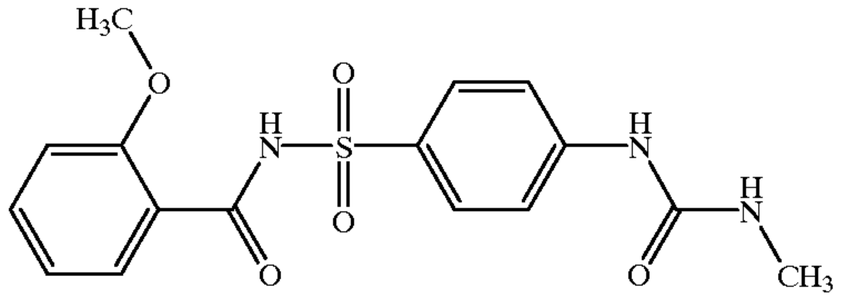
(2.05)



(3.03)



(4.001)



4 Claims, No Drawings

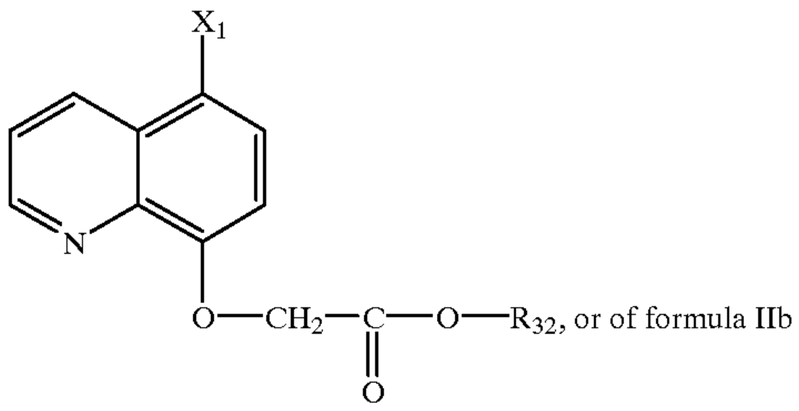
HERBICIDAL COMPOSITION

The present invention relates to new selectively herbicidal compositions to combat grasses and weeds in crops of cultivated plants, especially in crops of cereals and rice which comprise a herbicide and a safener (antidote) and which protect the cultivated plants but not the weeds against the phytotoxic effect of the herbicide, and to the use of this composition for weed control in crops of cultivated plants.

When applying herbicides, the cultivated plants may also suffer severe damage owing to factors that include the concentration of the herbicide and the mode of application, the cultivated plant itself, the nature of the soil, and the climatic conditions such as exposure to light, temperature and rainfall.

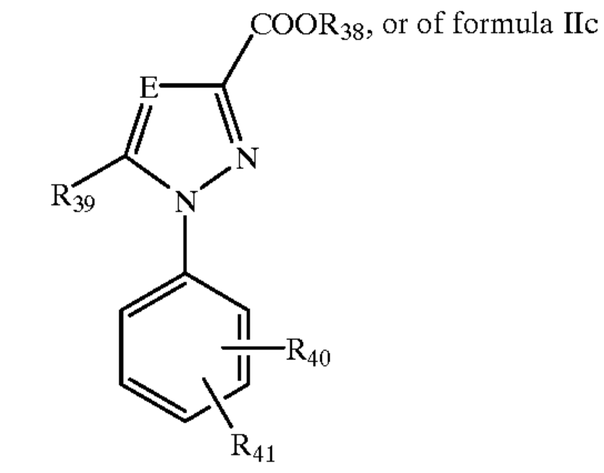
To counteract this problem and similar ones, the proposal has already been made to use different compounds as safeners which are able to antagonise the harmful action of the herbicide on the cultivated plant, i.e. to protect the cultivated plant while leaving the herbicidal action on the weeds to be controlled virtually unimpaired. It has, however, been found that the proposed safeners often have a very specific action with respect not only to the cultivated plants but also to the herbicide, and in some cases also subject to the mode of application, i.e. a specific safener will often be suitable only for a specific cultivated plant and a specific class of herbicide or a specific herbicide. Compounds are known for example from WO 97/18712 which protect crop plants against the phytotoxic effect of specific herbicides. It has now been found that compounds of formula

(IIa)

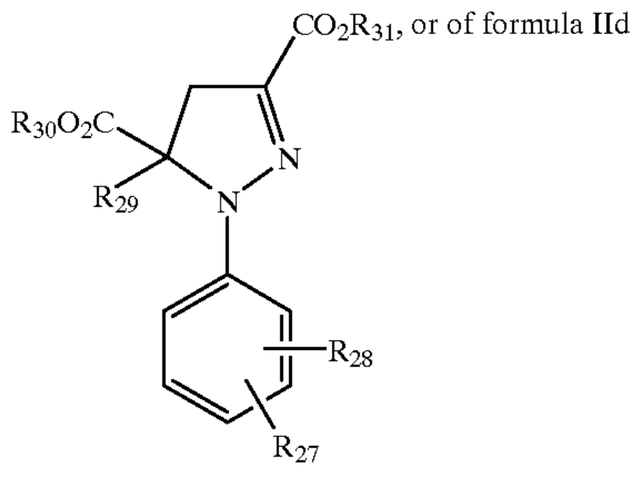


IIa

(IIb)



(IIc)



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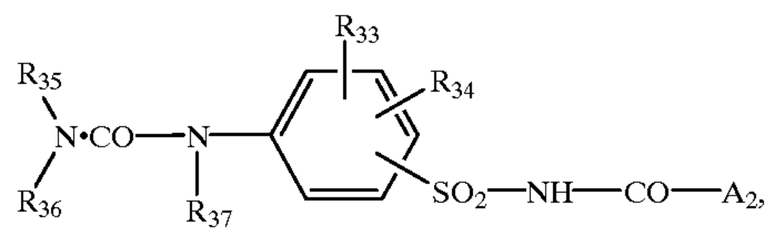
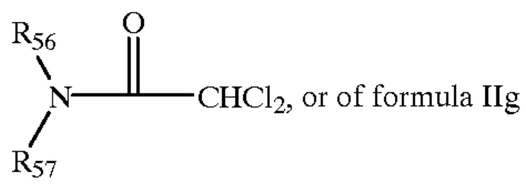
(IId)

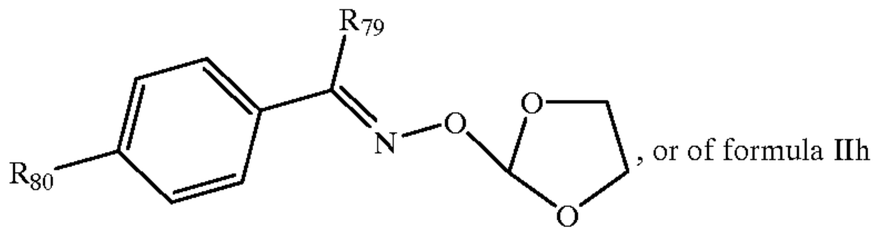


or of formula IIf

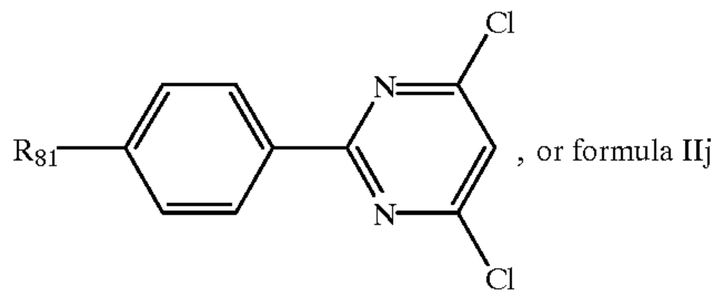
(IIf)



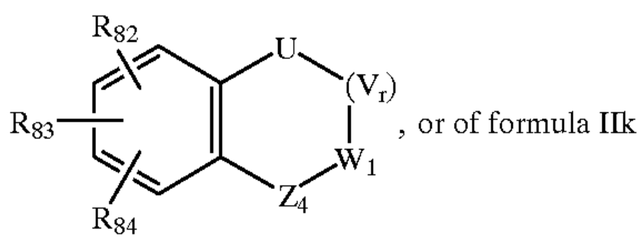
(IIg)



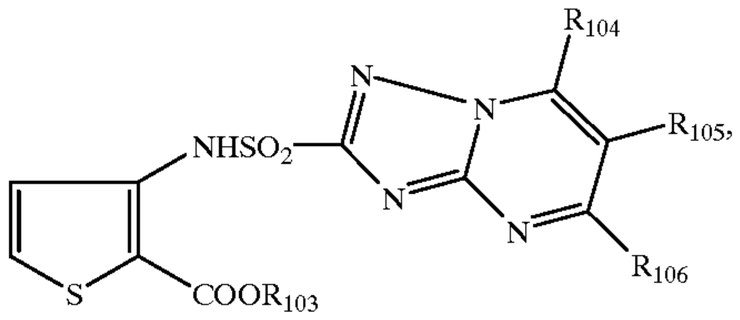
(IIh)



(IIj)

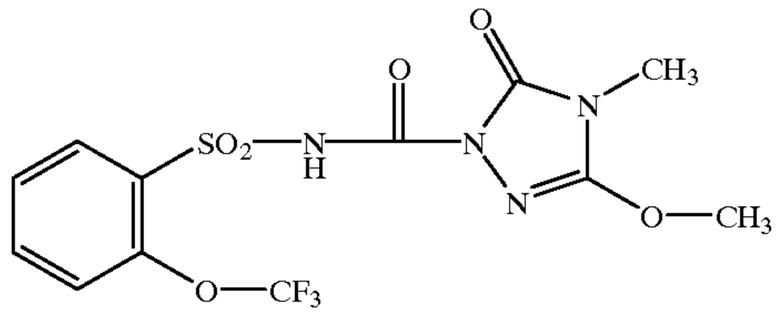


(IIk)



wherein the substituents are as defined hereinafter, are suitable for the protection of crop plants against the phytotoxic effect of a compound of formula I

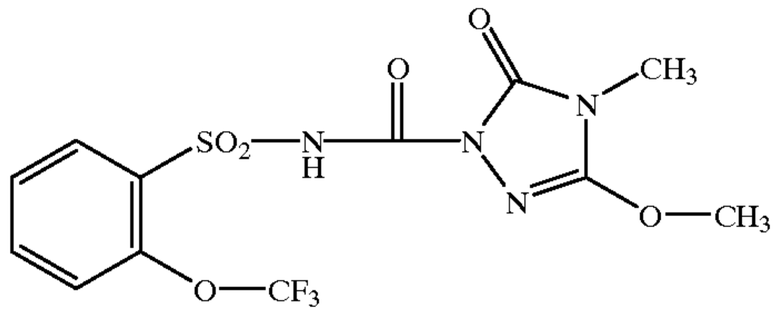
(I)



Accordingly, the invention provides a selective herbicidal composition comprising, in addition to customary inert formulation assistants such as carriers, solvents and wetting agents, a mixture of

a) a herbicidally effective amount of a herbicide of formula I

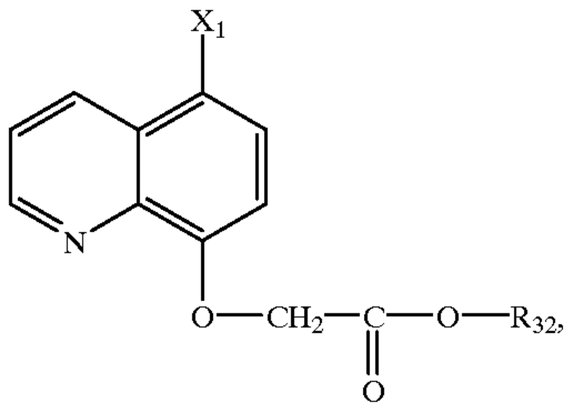
(I)



and

b) to antagonise the herbicide, an antidotally effective amount of a safener of formula IIa

(IIa)

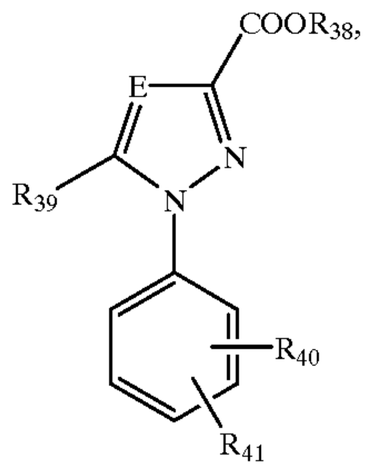


wherein

R_{32} is hydrogen, C_1–C_8alkyl or C_1–C_8alkyl substituted by C_1–C_6alkoxy or C_3–C_6alkenyloxy and

X_1 is hydrogen or chlorine; or of formula IIb

(IIb)



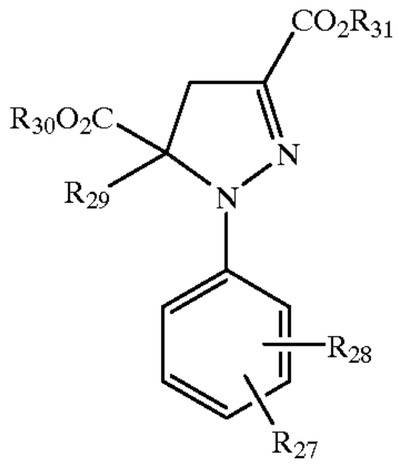
wherein E is nitrogen or methine;

R_{38} is C_1–C_4alkyl;

R_{39} is —CCl_3, phenyl or phenyl substituted by halogen, and

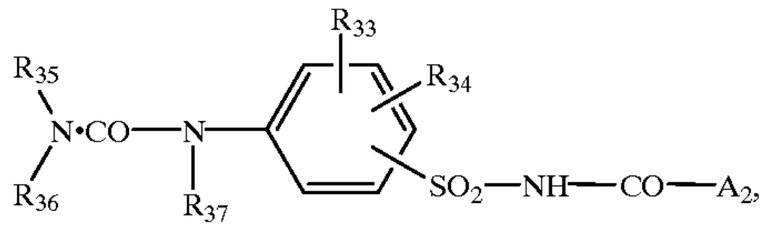
R_{40} and R_{41} independently of one another are hydrogen or halogen; or of formula IIc

(IIc)



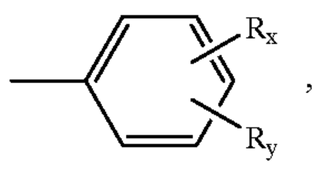
wherein R_{27} and R_{28} independently of one another are hydrogen or halogen, and R_{29}, R_{30} and R_{31} independently of one another are C_1–C_4alkyl; or of formula IId

(IId)

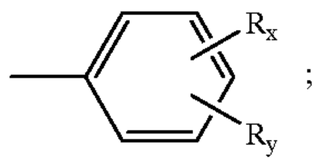


wherein A_2 is a

group, R_{35} and R_{36} independently of one another are hydrogen, C_1–C_8alkyl, C_3–C_8cycloalkyl, C_3–C_6alkenyl, C_3–C_6alkinyl,



or C_1–C_4alkyl substituted by C_1–C_4alkoxy or;



or R_{35} and R_{36} together form a C_4–C_6alkylene bridge, which may be broken by oxygen, sulfur, SO, SO_2, NH or —N(C_1–C_4alkyl)—; R_{37} is hydrogen or C_1–C_4alkyl;

R_{33} is hydrogen, halogen, cyano, trifluoromethyl, nitro, C_1–C_4alkyl, C_1–C_4alkoxy, C_1–C_4alkylthio, C_1–C_4alkylsulfinyl, C_1–C_4alkylsulfonyl, —$COOR_j$, —$CONR_kR_m$, —COR_n, —$SO_2NR_kR_m$ or —OSO_2—C_1–C_4alkyl;

R_g is hydrogen, halogen, cyano, nitro, C_1–C_4alkyl, C_1–C_4halogenalkyl, C_1–C_4alkylthio, C_1–C_4alkylsulfinyl, C_1–C_4alkylsulfonyl, —$COOR_j$, —$CONR_kR_m$, —COR_n, —$SO_2NR_kR_m$—OSO_2—C_1–C_4alkyl, C_1–C_6alkoxy, or C_1–C_6alkoxy substituted by C_1–C_4alkoxy or halogen, C_3–C_6alkenyloxy, or C_3–C_6alkenyloxy substituted by halogen, or C_3–C_6alkinyloxy, or R_{33} and R_{34} together form a C_3–C_4alkylene bridge, which may be substituted

by halogen or C_1–C_4alkyl, or they form a C_3–C_4alkenylene bridge, which may be substituted by halogen or C_1–C_4alkyl, or they form a C_4alkadienylene bridge, which may be substituted by halogen or C_1–C_4alkyl;

R_{34} and R_h independently of one another are hydrogen, halogen, C_1–C_4alkyl, trifluoromethyl, C_1–C_6alkoxy, C_1–C_6alkylthio or —$COOR_j$;

R_c is hydrogen, halogen, nitro, C_1–C_4alkyl or methoxy; R_d is hydrogen, halogen, nitro, C_1–C_4alkyl, C_1–C_4alkoxy, C_1–C_4alkylthio, C_1–C_4alkylsulfinyl, C_1–C_4alkylsulfonyl, —$COOR_j$ or $CONR_kR_m$;

R_e is hydrogen, halogen, C_1–C_4alkyl, —$COOR_j$, trifluoromethyl or methoxy, or R_d and R_e together form a C_3–C_4alkylene bridge;

R_f is hydrogen, halogen or C_1–C_4alkyl;

R_x and R_y independently of one another are hydrogen, halogen, C_1–C_4alkyl, C_1–C_4alkoxy, C_1–C_4alkylthio, —$COOR_{38}$, trifluoromethyl, nitro or cyano;

R_j, R_k and R_m independently of one another are hydrogen or C_1–C_4alkyl; or

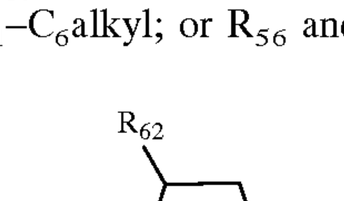
R_k and R_m together form a C_4–C_6alkylene bridge, which may be broken by oxygen, NH or —N(C_1–C_4alkyl)—;

R_n is C_1–C_4alkyl, phenyl, or phenyl substituted by halogen, C_1–C_4alkyl, methoxy, nitro or trifluoromethyl;

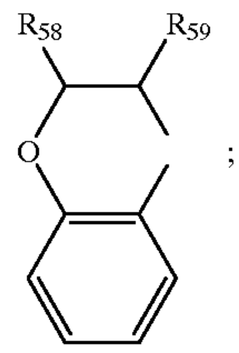
R_{38} is hydrogen, C_1–C_{10}alkyl, C_1–C_4alkoxy-C_1–C_4alkyl, C_1–C_4alkylthio-C_1–C_4alkyl, di-C_1–C_4alkylamino-C_1–C_4alkyl, halogen-C_1–C_8alkyl, C_2–C_8alkenyl, halogen-C_2–C_8alkenyl, C_3–C_8alkinyl, C_3–C_7cycloalkyl, halogen-C_3–C_7-cycloalkyl, C_1–C_8alkylcarbonyl, allylcarbonyl, C_3–C_7cycloalkylcarbonyl, benzoyl which is unsubstituted or substituted on the phenyl ring up to three times identically or differently by halogen, C_1–C_4alkyl, halogen-C_1–C_4alkyl, halogen-C_1–C_4alkoxy or C_1–C_4alkoxy; or furoyl, thienyl; or C_1–C_4alkyl substituted by phenyl, halogenphenyl, C_1–C_4alkylphenyl, C_1–C_4alkoxyphenyl, halogen-C_1–C_4alkylphenyl, halogen-C_1–C_4alkoxyphenyl, C_1–C_6alkoxycarbonyl, C_1–C_4alkoxy-C_1–C_8alkoxycarbonyl, C_3–C_8alkenyloxycarbonyl, C_3–C_8alkinyloxycarbonyl, C_1–C_8alkylthiocarbonyl, C_3–C_8alkenylthiocarbonyl, C_3–C_8alkinylthiocarbonyl, carbamoyl, mono-C_1–C_4alkylaminocarbonyl, di-C_1–C_4alkylaminocarbonyl; or phenylaminocarbonyl, which is unsubstituted or substituted on the phenyl ring up to three times identically or differently by halogen, C_1–C_4alkyl, halogen-C_1–C_4alkyl, halogen-C_1–C_4alkoxy or C_1–C_4alkoxy, or once by cyano or nitro, or dioxolan-2-yl which is unsubstituted or substituted by one or two C_1–C_4alkyl radicals, or dioxan-2-yl, which is unsubstituted or substituted by one or two C_1–C_4alkyl radicals, or C_1–C_4alkyl which is substituted by cyano, nitro, carboxyl or C_1–C_8alkylthio-C_1–C_8alkoxycarbonyl;

or a compound of formula IIf

(IIf)

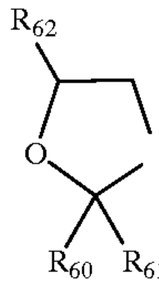


wherein R_{56} and R_{57} independently of one another are C_1–C_6alkyl or C_2–C_6alkenyl; or R_{56} and R_{57} together are;



;

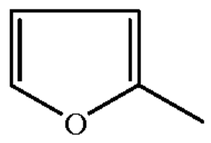
R_{58} and R_{59} independently of one another are hydrogen or C_1–C_6alkyl; or R_{56} and R_{57} together are;



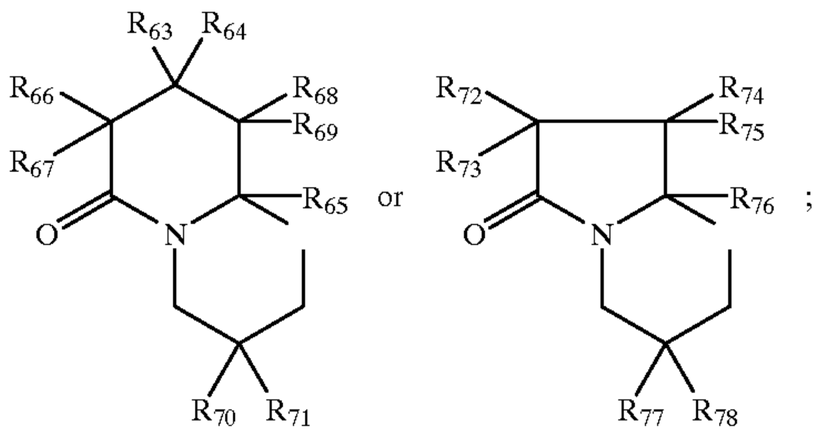
;

R_{60} and R_{61} independently of one another are C_1–C_4alkyl, or R_{46} and R_{47} together are —$(CH_2)_5$—;

R_{62} is hydrogen, C_1–C_4alkyl or

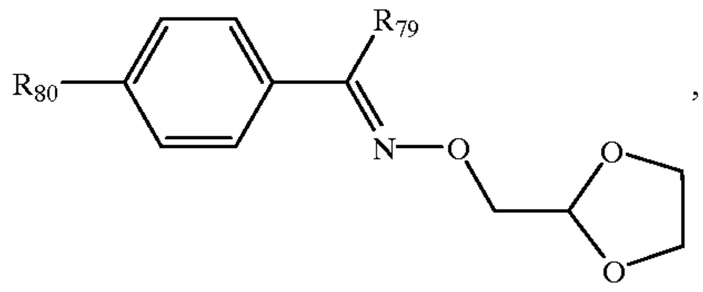


or R_{56} and R_{57} together are;



R_{63}, R_{64}, R_{65}, R_{66}, R_{67}, R_{68}, R_{69}, R_{70}, R_{71}, R_{72}, R_{73}, R_{74}, R_{75}, R_{76}, R_{77} and R_{78} independently of one another are hydrogen or C_1–C_4alkyl;

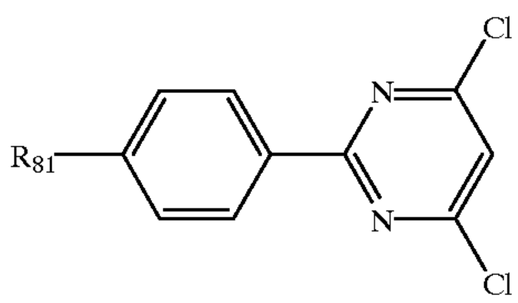
or a compound of formula IIg



(IIg)

wherein R_{79} is hydrogen or chlorine and R_{80} is cyano or trifluoromethyl,

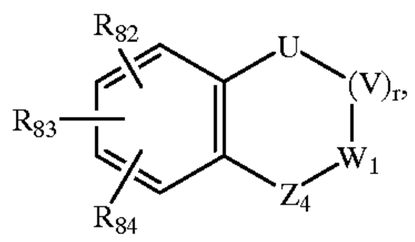
or a compound of formula IIh



(IIh)

wherein R_{81} is hydrogen or methyl,

or of formula IIj



(IIj)

wherein

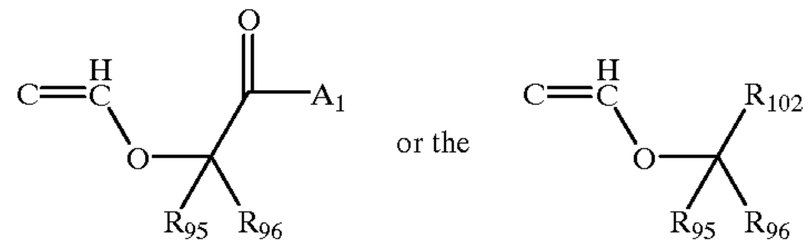
R_{82} is hydrogen, C_1–C_4alkyl, C_1–C_4alkyl substituted by C_1–C_4alkyl-X_2— or C_1–C_4halogenalkyl-X_2—, C_1–C_4halogenalkyl, nitro, cyano, —$COOR_5$, —$NR_{86}R_{87}$, —$SO_2NR_{88}R_{89}$ or —$CONR_{90}R_{91}$;

R_{83} is hydrogen, halogen, C_1–C_4alkyl, trifluoromethyl, C_1–C_4alkoxy or C_1–C_4halogenalkoxy;

R_{84} is hydrogen, halogen or C_1–C_4alkyl;

U, V, W_1 and Z_4 independently of one another are oxygen, sulfur, $C(R_{92})R_{93}$, carbonyl, NR_{94},

group, wherein R_{102} is C_2–C_4alkenyl or C_2–C_4alkinyl; subject to the proviso that a) at least one of the ring members U, V, W_1 or Z_4 is carbonyl, and a ring member adjacent to this or these ring members is either the



group, this group only occurring once; and

b) two adjacent ring members U and V, V and W_1 and W_1 and Z_4 cannot simultaneously be oxygen;

R_{95} and R_{96} independently of one another are hydrogen or C_1–C_8alkyl; or

R_{95} and R_{96} together form a C_2–C_6alkylene group;

A_1 is R_{99}—Y_1— or —$NR_{97}R_{98}$;

X_2 is oxygen or —$S(O)_s$;

Y_1 is oxygen or sulfur;

R_{99} is hydrogen, C_1–C_8alkyl, C_1–C_8halogenalkyl, C_1–C_4alkoxy-C_1–C_8alkyl, C_3–C_6alkenyloxy-C_1–C_8-alkyl or phenyl-C_1–C_8-alkyl, wherein the phenyl ring may be substituted by halogen, C_1–C_4—a, trifluoromethyl, methoxy or methyl—$S(O)_s$—, C_3–C_6alkenyl, C_3–C_6halogenalkenyl, phenyl-C_3–C_6alkenyl, C_3–C_6alkinyl, p-C_3–C_6alkinyl, oxetanyl, furyl or tetrahydrofuryl;

R_{85} is hydrogen or C_1–C_4alkyl;

R_{86} is hydrogen, C_1–C_4alkyl or C_1–C_4alkylcarbonyl;

R_{87} is hydrogen or C_1–C_4alkyl; or

R_{86} and R_{87} together form a C_4 or C_5alkylene group;

R_{88}, R_{89}, R_{90} and R_{91} independently of one another are hydrogen or C_1–C_4alkyl; or R_{88} and R_{89} or R_{90} and R_{91} are independently of one another C_4 or C_5alkylene, in which a carbon atom may be substituted by oxygen or sulfur, or one or two carbon atoms by —NR_{100}—;

R_{92} and R_{100} independently of one another are hydrogen or C_1–C_8alkyl; or

R_{92} and R_{93} together are C_2–C_6alkylene;

R_{94} is hydrogen or C_1–C_8alkyl;

R_{97} is hydrogen, C_1–C_8alkyl, phenyl, phenyl-C_1–C_8alkyl (in which the phenyl ring may be substituted by fluorine, chlorine, bromine, nitro, cyano, —OCH_3, C_1–C_4alkyl or CH_3SO_2—), C_1–C_4alkoxy-C_1–C_8alkyl, C_3–C_6alkenyl or C_3–C_6alkinyl;

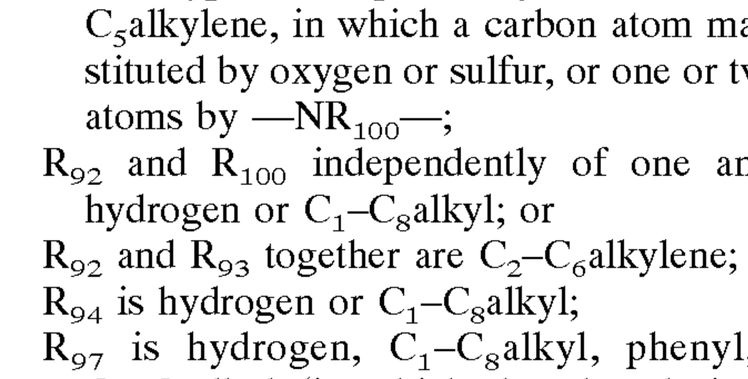
R_{98} is hydrogen, C_1–C_8alkyl, C_3–C_6alkenyl or C_3–C_6alkinyl; or

R_{97} and R_{98} together are C_4 or C_5alkylene, in which a carbon atom may be substituted by oxygen or sulfur, or one or two carbon atoms by —NR_{101}—;

R_{101} is hydrogen or C_1–C_4alkyl;

r is 0 or 1; and

s is 0, 1 or 2, or a compound of formula IIk



(IIk)

wherein R_{103} is hydrogen, C_1–C_6alkyl, C_3–C_6cycloalkyl, C_3–C_6alkenyl or C_3–C_6alkinyl;

and R_{104}, R_{105} and R_{106} are independently of one another hydrogen, C_1–C_6alkyl, C_3–C_6cycloalkyl or C_1–C_6alkoxy, subject to the proviso that one of the substituents R_{104}, R_{105} or R_{106} is different from hydrogen.

The alkyl groups occurring in the substituent definitions may be straight-chained or branched, and may for example be methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl or octyl, as well as their branched isomers. Alkoxy, alkylthio, alkoxycarbonyl, alkylcarbonyl, alkylsulfonyl, and alkylsulfinyl groups are derived from the said alkyl groups. Halogen is usually fluorine, chlorine, bromine or iodine, preferably fluorine, chlorine or bromine. In substituents such as —NR_kR_m, the alkyl radicals may be the same or different. In the preferred embodiment, they are the same. The term "substituted" may mean in the context of the present invention monosubstituted and, as far as possible, also polysubstituted.

The compound of formula 1 is described in EP-A-0 507 171. Compounds of formulae IIa, IIb, IIc, IId, IIf, IIg, IIh, IIj, and IIk are known from U.S. Pat. No. 5,041,157, U.S. Pat. No. 5,541,148, U.S. Pat. No. 5,006,656, EP-A-0 094 349, EP-A-0 551 650, EP-A-0 268 554, EP-A-0 375 061, EP-A-0 174 562, EP-A-492 366, WO 91/7874, WO 941987, DE-A-19612943, WO 96/29870, WO 98/13361, and WO 97/18712.

The compound of formula I may preferably be used according to the invention with the safeners of formulae IIa, IIb and IIc.

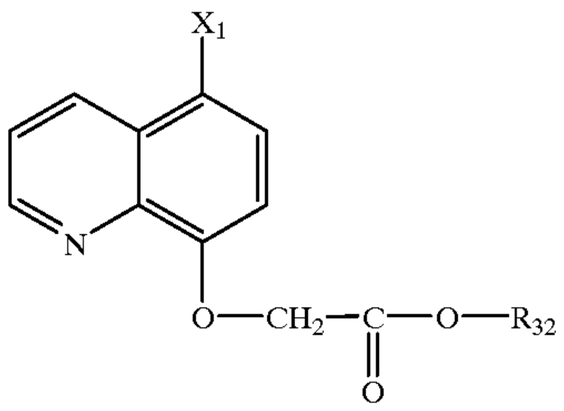
A very especially preferred composition according to the invention comprises the compound of formula I and the safener of formula IIa, wherein XI is chlorine and R_{22}. is —$CH(CH_3)C_5H_{11}$—n.

Especially preferred compounds of the formulae and IIa to IIk are listed in the following tables (formula IIe is the preferred compound of formula IId, and formulae IIm, IIn, IIo and IIp are the preferred compounds of formula IIh):

TABLE 1

Compounds of formula IIa:

(IIa)

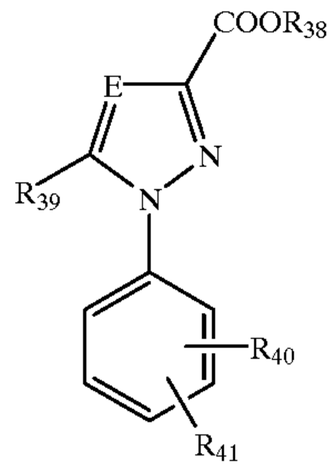


Comp. no.	X_1	R_{32}
1.01	Cl	—$CH(CH_3)$—C_5H_{11}-n
1.02	Cl	—$CH(CH_3)$—CH_2OCH_2CH=CH_2
1.03	Cl	H
1.04	Cl	C_4H_9-n

TABLE 2

Compounds of formula IIb:

(IIb)

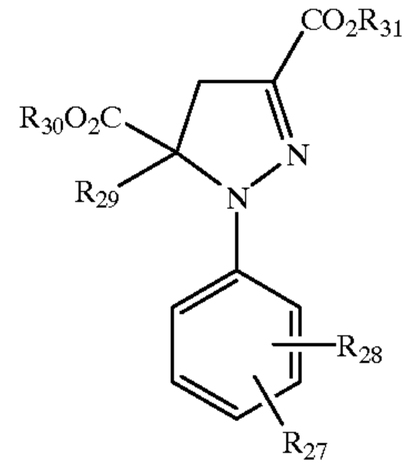


Comp. no.	R_{38}	R_{39}	R_{40}	R_{41}	E
2.01	CH_3	Phenyl	2-Cl	H	CH
2.02	CH_3	Phenyl	2-Cl	4-Cl	CH
2.03	CH_3	Phenyl	2-F	H	CH
2.04	CH_3	2-Chlorophenyl	2-F	H	CH
2.05	C_2H_5	CCl_3	2-Cl	4-Cl	N
2.06	CH_3	Phenyl	2-Cl	4-CF_3	N
2.07	CH_3	Phenyl	2-Cl	4-CF_3	N
2.08	CH_3	2-Fluorophenyl	2-Cl	H	CH

TABLE 3

Compound of formula IIc

(IIc)

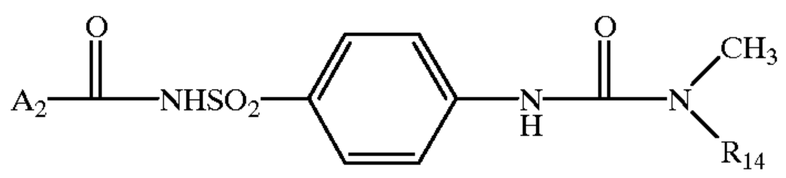


Comp. no.	R_{29}	R_{30}	R_{31}	R_{27}	R_{28}
3.01	CH_3	CH_3	CH_3	2-Cl	4-Cl
3.02	CH_3	C_2H_5	CH_3	2-Cl	4-Cl
3.03	CH_3	C_2H_5	C_2H_5	2-Cl	4-Cl

TABLE 4

Compounds of formula IIe:

(IIe)



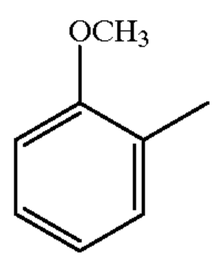
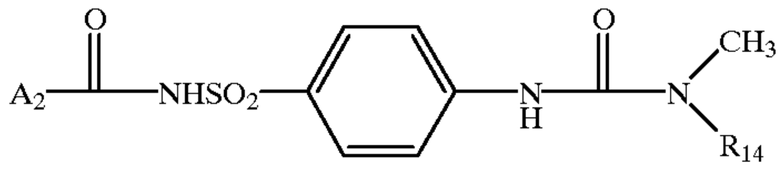
Comp. no.	A_2	R_{14}
4.001		H

TABLE 4-continued

Compounds of formula IIe:

(IIe)



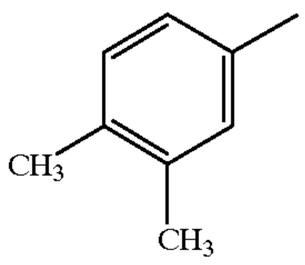
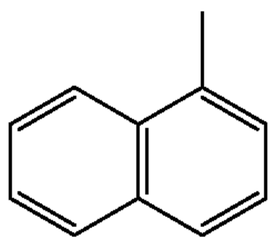
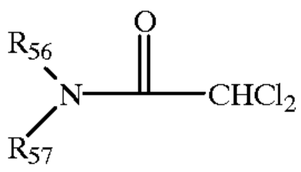
Comp. no.	A_2	R_{14}
4.002		H
4.003		CH_3
4.004		CH_3

TABLE 5

Compounds of formula IIf:

(IIf)



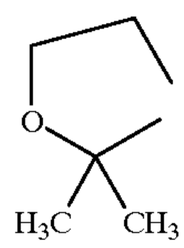
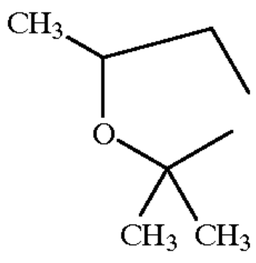
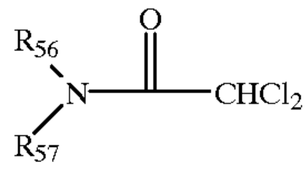
Comp. no.	R_{56}	R_{57}	$R_{56} + R_{57}$
5.001	CH_2=$CHCH_2$	CH_2=$CHCH_2$	—
5.002	—	—	
5.003	—	—	

TABLE 5-continued

Compounds of formula IIf:

(IIf)



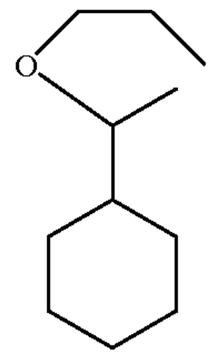
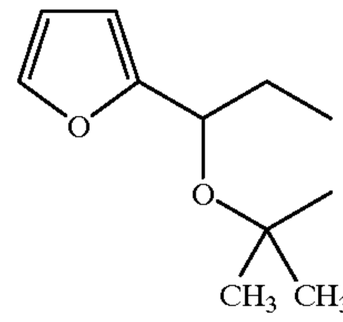
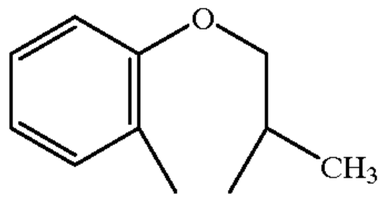
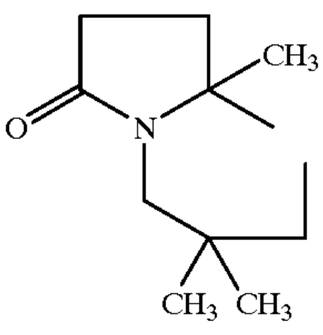
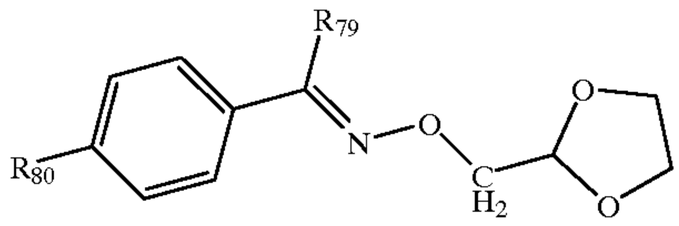
Comp. no.	R_{56}	R_{57}	$R_{56} + R_{57}$
5.004	—	—	
5.005	—	—	
5.006	—	—	
5.007	—	—	

TABLE 6

Compounds of formula IIg:

(IIg)

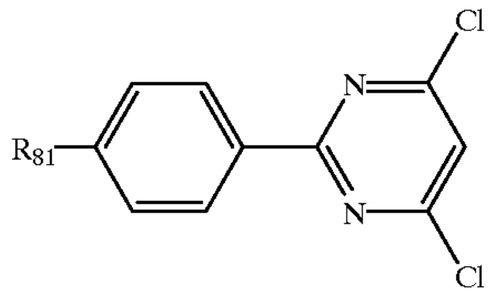


Comp. no.	R_{80}	R_{79}
6.01	H	CN
6.02	Cl	CF_3

TABLE 7

Compounds of formula IIh:

(IIh)

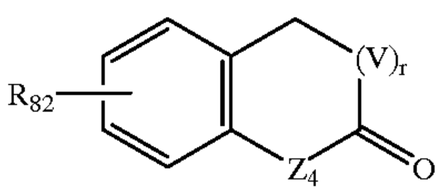


Comp. no.	R_{81}
7.01	H
7.02	CH_3

TABLE 8

Compounds of formula IIm

(IIm)



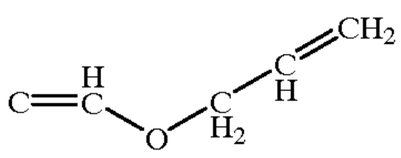
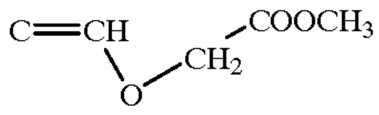
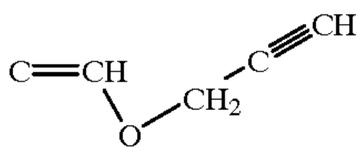
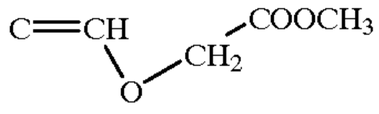
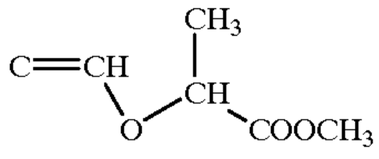
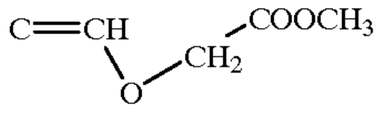
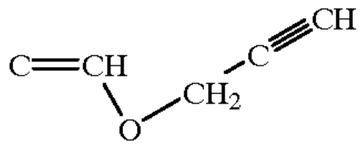
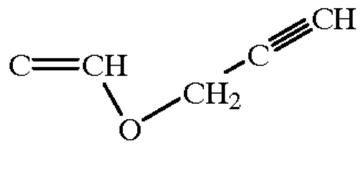
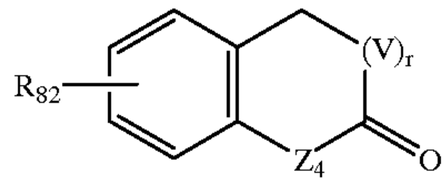
Comp. no.	R_{82}	Z_4	V	r
8.001	H		O	1
8.002	H		O	1
8.003	H		O	1
8.004	H		O	1
8.005	H		CH_2	1
8.006	H		CH_2	1
8.007	H		S	1
8.008	H		S	1
8.009	H		NCH_3	1

TABLE 8-continued

Compounds of formula IIm

(IIm)



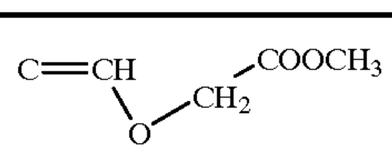
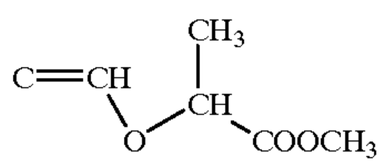
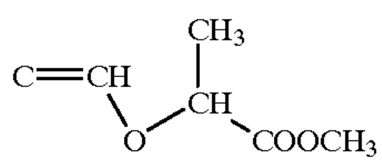
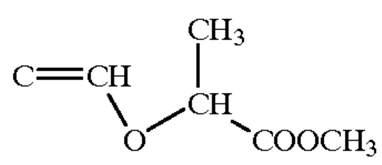
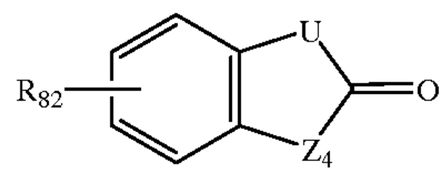
Comp. no.	R_{82}	Z_4	V	r
8.010	H		NCH_3	1
8.011	H		NCH_3	1
8.012	H		O	1
8.013	H		S	1

TABLE 9

Compounds of formula IIn

(IIn)



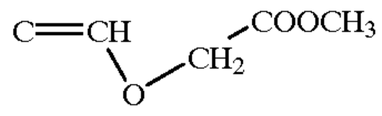
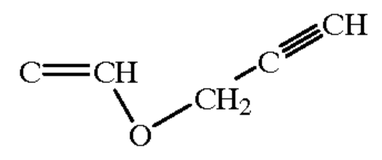
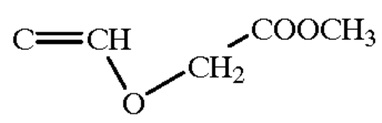
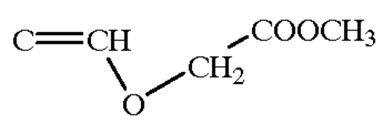
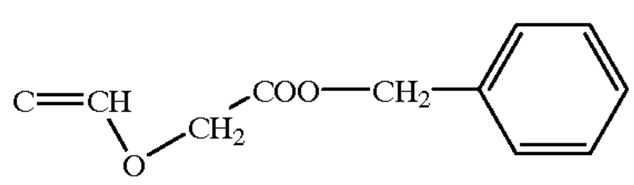
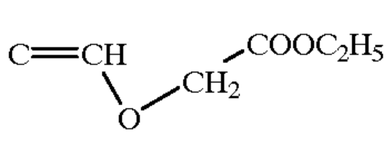
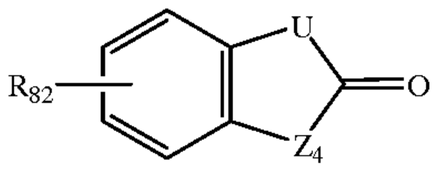
Comp. no.	U	R_{82}	Z_4
9.001	O	H	
9.002	O	H	
9.003	O	5-Cl	
9.004	CH_2	H	
9.005	CH_2	H	
9.006	CH_2	H	

TABLE 9-continued

Compounds of formula IIn

(IIn)



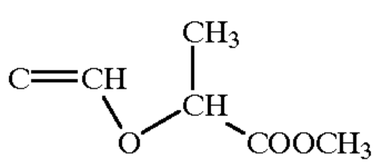
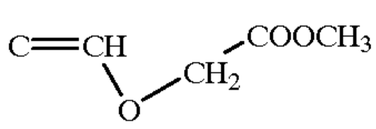
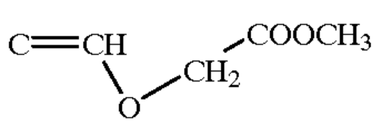
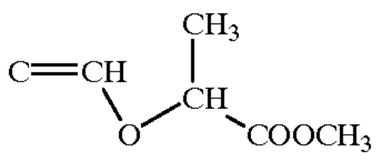
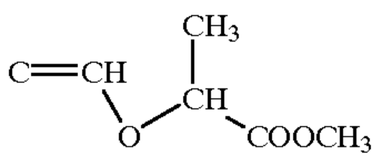
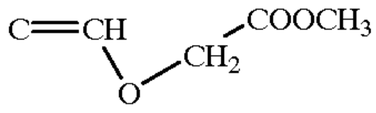
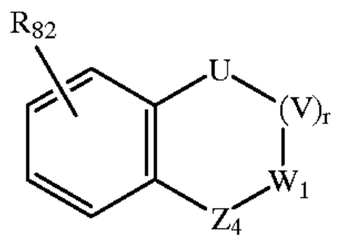
Comp. no.	U	R_{82}	Z_4
9.007	NH	5-Cl	
9.008	NH	5-Cl	
9.009	NH	H	
9.010	NH	H	
9.011	NCH_3	H	
9.012	NCH_3	H	

TABLE 10

Compounds of formula IIo

(IIo)



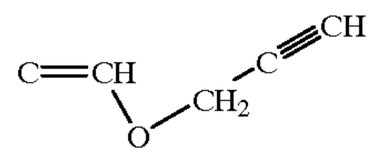
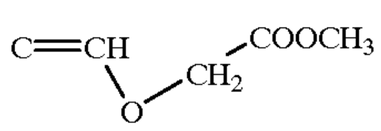
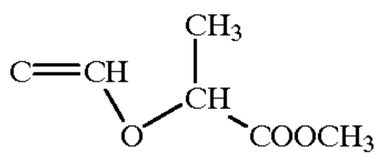
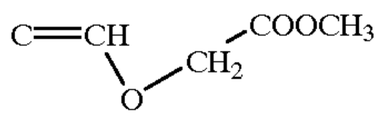
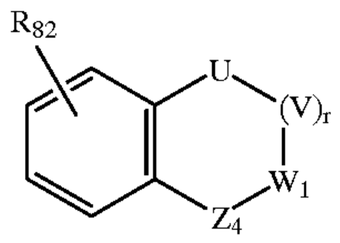
Comp. no.	U	V	r	W_1	Z_4	R_{82}
10.001	0	C═O	1		CH_2	H
10.002	O	C═O	1		CH_2	H
10.003	CH_2	C═O	1		CH_2	H
10.004	CH_2	C═O	1		CH_2	H

TABLE 10-continued

Compounds of formula IIo

(IIo)



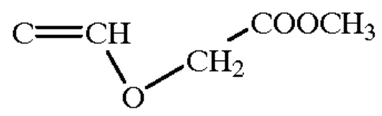
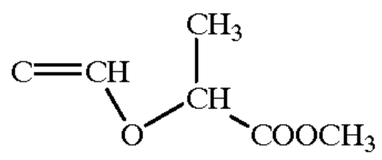
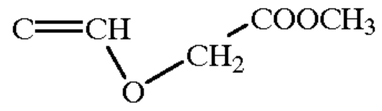
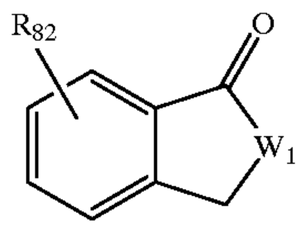
Comp. no.	U	V	r	W_1	Z_4	R_{82}
10.005	CH_2	CH_2	1		C═O	H
10.006	CH_2	CH_2	1		C═O	H
10.007	NCH_3	C═O	1		CH_2	H

TABLE 11

Compounds of formula IIp

(IIp)



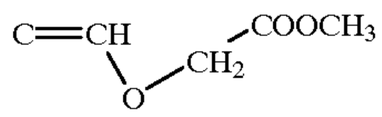
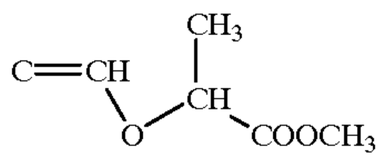
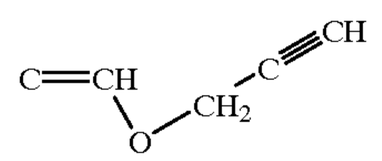
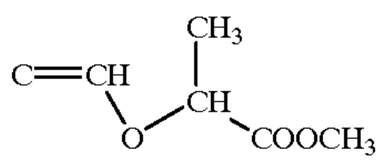
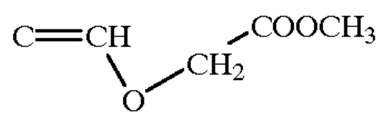
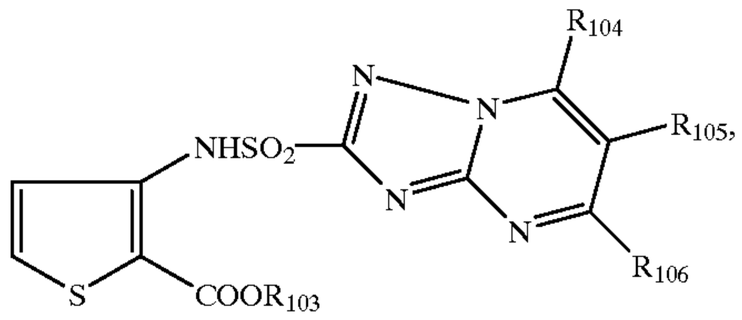
Comp. no.	R_{82}	W_1
11.001	6-Cl	
11.002	6-Cl	
11.003	H	
11.004	H	
11.005	H	

TABLE 12

Compounds of formula IIk

(IIk)



Comp no.	R_{103}	R_{104}	R_{105}	R_{106}
12.01	CH_3	H	Cyclopropyl	H
12.02	CH_3	C_2H_5	Cyclopropyl	H
12.03	CH_3	Cyclopropyl	C_2H_5	H
12.04	CH_3	CH_3	H	H
12.05	CH_3	CH_3	Cyclopropyl	H
12.06	CH_3	OCH_3	OCH_3	H
12.07	CH_3	CH_3	OCH_3	H
12.08	CH_3	OCH_3	CH_3	H
12.09	CH_3	CH_3	CH_3	H
12.10	C_2H_5	CH_3	CH_3	H
12.11	C_2H_5	OCH_3	OCH_3	H
12.12	H	OCH_3	OCH_3	H
12.13	H	CH_3	CH_3	H
12.14	C_2H_5	H	H	CH_3
12.15	H	H	H	CH_3
12.16	CH_3	H	H	CH_3

The invention also relates to a method of selectively controlling weeds in crops of cultivated plants, which comprises treating said cultivated plants, the seeds or seedlings or the crop area thereof, concurrently or separately, with a herbicidally effective amount of the herbicide of formula I and, to antagonise the herbicide, an antidotally effective amount of the safener of formula IIa, IIb, IIc IId, IIf, IIg, IIh, IIj or IIk.

Crop plants which may be protected by the safeners of formula IIa, IIb, IIc IId, IIf, IIg, IIh, IIj or IIk from the damaging effect of the herbicides mentioned hereinbefore are in particular cereals and rice. Crops will also be understood as meaning those crops that have been made tolerant to herbicides or classes of herbicides by conventional breeding or genetic engineering methods.

The weeds to be controlled may be monocot as well as dicot weeds, typically Stellaria, Nasturtium, Agrostis, Digitaria, Avena, Setaria, Sinapis, Lolium, Solanum, Echinochloa, Scirpus, Monochoria, Sagittaria, Bromus, Alopecurus, *Sorghum halepense*, Rottboellia, Cyperus, Abutilon, Sida, Xanthium, Amaranthus, Chenopodium, lpomoea, Chrysanthemum, Galium, Viola, and Veronica.

Crop areas will be understood as meaning the areas already under cultivation with the cultivated plants or seeds thereof, as well as the areas intended for cropping with said cultivated plants.

Depending on the end use, a safener of formula II can be used for pretreating seeds of the crop plants (dressing of seeds or seedlings) or it can be incorporated in the soil before or after sowing. It can, however, also be applied by itself alone or together with the herbicide postemergence. Treatment of the plant or the seeds with the safener can therefore in principle be carried out irrespective of the time of application of the herbicide. Treatment can, however, also be carried out by simultaneous application of the phytotoxic chemical and safener (e.g. as tank mixture). The concentration of safener with respect to the herbicide will depend substantially on the mode of application. Where a field treatment is carried out either by using a tank mixture with a combination of safener and herbicide or by separate application of safener and herbicide, the ratio of safener to herbicide will usually be from 1:100 to 1:1, and preferably 1:50 to 5:1.

In field treatment it is usual to apply 0.001 to 5.0 kg safener/ha, preferably 0.001 to 0.5 kg safener/ha.

The rate of application of herbicide is usually in the range from 0.001 to 2 kg/ha, but will preferably be from 0.005 to 1 kg/ha.

The compositions of this invention are suitable for all methods of application commonly used in agriculture, including preemergence application, postemergence application and seed dressing.

For seed dressing, 0.001 to 10 g of safener/kg of seeds, preferably 0.05 to 2 g of safener/kg of seeds, is usually applied. If the safener is used in liquid form shortly before sowing to effect soaking, then it is preferred to use safener solutions that contain the active ingredient in a concentration of 1 to 10000 ppm, preferably of 100 to 1000 ppm.

For application, it is expedient to process the safeners of formula II, or mixtures of the safeners of formula 11 and the herbicides of formula I, together with the customary assistants of formulation technology to formulations, typically to emulsifiable concentrates, coatable pastes, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts, granulates or microcapsules.

Such formulations are described, for example, in WO 97/34485 on pages 9 to 13. The formulations are prepared in known manner, for example by homogeneously mixing or grinding the active ingredients with liquid or solid formulation assistants, typically solvents or solid carriers. Surface-active compounds (surfactants) may additionally be used for preparing the formulations. Suitable solvents and solid carriers for this purpose are described in WO 97/34485 on page 6.

Depending on the herbicide of formula I to be formulated, suitable surface-active compounds are nonionic, cationic and/or anionic surfactants and surfactant mixtures having good emulsifying, dispersing and wetting properties. Examples of suitable anionic, nonionic, and cationic surfactants are listed in WO 97/34485 on pages 7 and 8. Also the surfactants customarily employed in the art of formulation and described, inter alia, in "Mc Cutcheon's Detergents and Emulsifiers Annual" MC Publishing Corp., Ridgewood N.J., 1981, Stache, H., "Tensid-Taschenbuch" (Handbook of Surfactants), Carl Hanser Verlag, Munich/Vienna, 1981, and M. and J. Ash, "Encyclopedia of Surfactants", Vol I–III, Chemical Publishing Co., New York, 1980–81 are suitable for manufacture of the herbicides according to the invention.

The herbicidal compositions will usually contain from 0.1 to 99% by weight, preferably from 0.1 to 95% by weight, of compound mixture of the compound of formula I and the compounds of formula IIa, IIb, IIc IId, IIf, IIg, IIh, IIj, or IIk, from 1 to 99.9% by weight of a solid or liquid formulation assistant, and from 0 to 25% by weight, preferably from 0.1 to 25% by weight, of a surfactant.

Whereas it is customarily preferred to formulate commercial products as concentrates, the end user will normally use dilute formulations.

The compositions may also contain further ingredients, such as: stabilisers, e.g. where appropriate epoxidised vegetable oils (epoxidised coconut oil, rapeseed oil, or soybean oil); antifoams, typically silicone oil; preservatives; viscosity regulators; binders; and tackifiers; as well as fertilisers or other chemical agents. Different methods and techniques may suitably be used for applying the safeners of formula II

or compositions containing them for protecting cultivated plants from the harmful effects of herbicides of formula I, conveniently the following:

i) Seed Dressing

a) Dressing the seeds with a wettable powder formulation of the active ingredient of formula II by shaking in a vessel until the safener is uniformly distributed on the surface of the seeds (dry treatment). About 1 to 500 g of active ingredient of formula IIa, IIb, IIc IId, IIf, IIg, IIh, IIj, or IIk (4 g to 2 kg of wettable powder) are used per 100 kg of seeds.

Dressing the seeds with an emulsifiable concentrate of the active ingredient of formula IIa, IIb, IIc IId, IIf, IIg, IIh, IIj, or IIk according to method a) (wet treatment).

c) Dressing by immersing the seeds in a mixture containing 100–1000 ppm of active ingredient of formula IIa, IIb, IIc IId, IIf, IIg, IIh, IIj, or IIk for 1 to 72 hours and, where appropriate, subsequently drying them (seed soaking).

In keeping with the natural environment, the preferred method of application is either seed dressing or treatment of the germinated seedlings, because the safener treatment is fully concentrated on the target crop. Usually 1 to 1000 g, preferably 5 to 250 g, of safener is used per 100 kg of seeds. However, depending on the method employed, which also permits the use of other chemical agents or micronutrients, the concentrations may deviate above or below the indicated limit values (repeat dressing).

ii) Application as a Tank Mixture

A liquid formulation of a mixture of safener and herbicide (reciprocal ratio from 10:1 to 1:100) is used, the concentration of herbicide being from 0.005 to 5.0 kg/ha. This tank mixture is applied before or after sowing.

iii) Application in the Furrow

The active ingredient of formula IIa, IIb, IIc IId, IIf, IIg, IIh, IIj, or IIk formulated as emulsifiable concentrate, wettable powder or granulate is applied to the open furrow in which the seeds have been sown. After covering the furrow, the herbicide is applied pre-emergence in conventional manner.

iv) Controlled Release of Compound

The compound of formula Formel IIa, IIb, IIc IId, IIf, IIg, IIh, IIj, or IIk is applied in solution to a mineral granular carrier or to polymerised granules (urea/formaldehyde) and then dried. A coating can then be applied (coated granules) that allows the herbicide to be released at a controlled rate over a specific period of time.

Particularly preferred formulations are made up as follows: (%=per cent by weight)

Emulsifiable concentrates:	
Compound mixture	1 to 90%, preferably 5 to 20%
Surfactant	1 to 30%, preferably 10 to 20%
Liquid carrier	5 to 94%, preferably 70 to 85%
Dusts:	
Compound mixture	0.1 to 10%, preferably 0,1 to 5%
Solid carrier	99.9 to 90%, preferably 99,9 to 99%
Suspension concentrates:	
Compound mixture	5 to 75%, preferably 10 to 50%
Water	94 to 30%, preferably 88 to 20%
Surfactant	1 to 30%, preferably 2 to 20%
Wettable powders:	
Compound mixture	1 to 90%, preferably 10 to 80%
Surfactant	1 to 30%, preferably 10 to 20%
Solid carrier	5 to 95%, preferably 15 to 90%

-continued

Granulates:	
Compound mixture	0.1 to 30%, preferably 0,1 to 15%
Solid carrier	99.5 to 70%, preferably 97 to 85%

The invention is illustrated by the following non-limitative Examples. Formulation Examples for mixtures of herbicides of formula I and safeners of formula IIa, IIb, IIc IId, IIf, IIg, IIh, IIj, or IIk (%=per cent by weight)

F1. Emulsifiable concentrates	a)	b)	c)	d)
Compound mixture	5%	10%	25%	50%
Calcium dodecylbenzenesulfonate	6%	8%	6%	8%
Polyethoxylated castor oil (36 mol EO)	4%	—	4%	4%
Octylphenol polyethoxylate (7–8 mol EO)	—	4%	—	2%
Cyclohexanone	—	—	10%	20%
Arom. hydrocarbon mixture C_9–C_{12}	85%	78%	55%	16%

Emulsions of any desired concentration can be prepared by diluting such concentrates with water.

F2. Solutions	a)	b)	c)	d)
Compound mixture	5%	10%		50% 90%
1-Methoxy-3-(3-methoxy-propoxy)-propane	—	20%	20%	—
Polyethylene glycol MG 400	20%	10%	—	—
N-Methyl-2-pyrrolidone		—	—	30% 10%
Arom. hydrocarbon mixture C_9–C_{12}	75%	60%	—	—

The solutions are suitable for use in the form of micro-drops.

F3. Wettable powders	a)	b)	c)	d)
Compound mixture	5%	25%	50%	80%
Sodium ligninsulfonate		4%	—	3%—
Sodium lauryl sulfate	2%	3%	—	4%
Sodium diisobutylnaphthalene	—	6%	5%	6%
Octylphenol polyethoxylate (7–8 mol EO)	—	1%	2%	—
Highly dispersed silicic acid	1%	3%	5%	10%
Kaolin	88%	62%	35%	—

The compound is throughly mixed with the adjuvants and this mixture is ground in a suitable mill to give wettable powders which can be diluted with water to give suspensions of any desired concentration.

F4. Coated granulates	a)	b)	c)
Compound mixture	0.1%	5%	15%
Highly dispersed silicic acid	0.9%	2%	2%
Inorganic substrate (Æ0.1–1 mm) such as $CaCo_3$ or SiO_2	99.0%	93%	83%

The compound mixture is dissolved in dichloromethane, the solution is sprayed on to the carrier, and the solvent is removed under vacuum.

F5. Coated granulates	a)	b)	c)
Compound mixture	0.1%	5%	15%
Polyethylene glycol MG 200	1.0%	2%	3%
Highly dispersed silicic acid	0.9%	1%	2%
Inorganic substrate (Æ0.1–1 mm) such as $CaCO_3$ or SiO_2	98.0%	92%	80%

The finely ground active substance is uniformly applied in a mixer to the carrier moistened with polyethylene glycol. Non-dusty coated granulates are obtained in this manner.

F6. Extruder granulates	a)	b)	c)	d)
Compound mixture	0.1%	3%	5%	15%
Sodium ligninsulfonate	1.5%	2%	3%	4%
Carboxymethylcellulose	1.4%	2%	2%	2%
Kaolin	97.0%	93%	90%	79%

The compound is mixed and ground with the adjuvants, and the mixture is moistened with water. This mixture is extruded and then dried in a stream of air.

F7. Dusts	a)	b)	c)
Compound mixture	0.1%	1%	5%
Talc	39.9%	49%	35%
Kaolin	60.0%	50%	60%

Ready for use dusts are obtained by mixing the active ingredient with the carriers on a suitable mill.

F8. Suspension concentrates	a)	b)	c)	d)
Compound mixture	3%	10%	25%	50%
Ethylene glycol	5%	5%	5%	5%
Nonylphenol polyethoxylate (15 mol EO)	—	1%	2%	—
Sodium ligninsulfonate	3%	3%	4%	5%
Carboxymethylcellulose	1%	1%	1%	1%
37% aqueous formaldehyde solution	0.2%	0.2%	0.2%	0.2%
Silicone oil emulsion	0.8%	0.8%	0.8%	0.8%
Water	87%	79%	62%	38%

The finely ground active substance is intimately mixed with the adjuvants to give a suspension concentrate from which suspensions of any desired concentration can be prepared by dilution with water.

It is often expedient to formulate the compound of formula I and the components of formulae IIa to IIk individually and only to combine them shortly before application in the applicator in the desired mixture ratio as tank mixture in water.

The following Examples illustrate the ability of the safeners of formula IIa, IIb, IIc IId, IIf, IIg, IIh, IIj, or IIk to protect cultivated plants from the phytotoxic action of herbicides of formula I.

BIOLOGICAL EXAMPLES

Example B1

Post-emergent Applications of Mixtures of a Herbicide of Formula I with a Safener of Formulae IIa to IIk to Cereals.

Under greenhouse conditions, wheat is grown in plastic pots to the 2.5-leaf stage. In this stage, both the herbicide of formula I alone and the mixture of the herbicide with a safener of formulae IIa to IIk are applied to the test plants. The test substances (Formulation Examples F3 a) and b)) are applied as aqueous suspension with 500 l water/ha. Ten days after the application, the results are evaluated on a percent scale. The results obtained show that, with the safeners of formulae IIa to IIk, the damage caused to wheat can be markedly reduced by the herbicide of formula I.

Examples of the selective effect of the compositions of the invention are given in Tables B1 to B4:

TABLE B1

Plant:	Herbicide of formula 1: 60 g/ha	Herbicide of formula 1: 60 g/ha Safener no. 6.02: 15 g/ha
Wheat	20	10
Chenopodium	90	80
Emex	90	90
Raphanus	80	80
Setaria	80	80

TABLE B2

Plant:	Herbicide of formula 1: 15 g/ha	Herbicide of formula 1: 15 g/ha Safener no. 1,01: 4 g/ha
Wheat	10	5
Chenopodium	90	90
Emex	80	90
Raphanus	80	80
Setaria	70	70

TABLE B3

Plant:	Herbicide of formula 1: 15 g/ha	Herbicide of formula 1: 15 g/ha Safener no. 4.001: 4 g/ha
Wheat	10	5
Chenopodium	80	80
Emex	80	90
Raphanus	80	80
Setaria	70	80

TABLE B4

Plant:	Herbicide of formula 1: 15 g/ha	Herbicide of formula 1: 15 g/ha Safener no. 3,03: 4 g/ha
Wheat	10	5
Chenopodium	90	90
Emex	80	90
Raphanus	80	80
Setaria	70	70

The same results are obtained by formulating a compound of formulae I and IIa to IIk in accordance with Examples F1, F2 and F4 to F7.

Example B2

Post-emergent Applications of Mixtures of a Herbicide of Formula I with a Safener of Formulae IIa to IIk to Barley.

Under greenhouse conditions, barley is grown in plastic pots to the 2.5-leaf stage. In this stage, both the herbicide of formula I alone and the mixture of the herbicide with a safener of formulae IIa to IIk are applied to the test plants. The test substances (Formulation Examples F3 a) and b)) are applied as aqueous suspension with 500 l water/ha. Ten days after the application, the results are evaluated on a percent scale. The results obtained show that, with the safeners of formulae IIa to IIk, the damage caused to barley can be markedly reduced by the herbicide of formula I.

Examples of the selective effect of the compositions of the invention are given in Tables B5 to B11:

TABLE B5

Plant:	Herbicide of formula 1: 60 g/ha	Herbicide of formula 1: 60 g/ha Safener no. 3,03: 15 g/ha
Barley	40	30
Chenopodium	90	80
Emex	90	90
Raphanus	80	80
Setaria	80	80

TABLE B6

Plant:	Herbicide of formula 1: 60 g/ha	Herbicide of formula 1: 60 g/ha Safener no. 6.02: 15 g/ha
Barley	40	30
Chenopodium	90	80
Emex	90	90
Raphanus	80	80
Setaria	80	80

TABLE B7

Plant:	Herbicide of formula 1: 60 g/ha	Herbicide of formula 1: 60 g/ha Safener no. 4.001: 15 g/ha
Barley	40	30
Chenopodium	90	80
Emex	90	90
Raphanus	80	80
Setaria	80	80

TABLE B8

Plant:	Herbicide of formula 1: 60 g/ha	Herbicide of formula 1: 60 g/ha Safener no. 2,05: 15 g/ha
Barley	40	30
Chenopodium	90	90
Emex	90	90
Raphanus	80	90
Setaria	80	80

TABLE B9

Plant:	Herbicide of formula 1: 60 g/ha	Herbicide of formula 1: 60 g/ha Safener no. 2,01: 15 g/ha
Barley	40	10
Chenopodium	90	90
Emex	90	90
Raphanus	80	80
Setaria	80	70

TABLE B10

Plant:	Herbicide of formula 1: 15 g/ha	Herbicide of formula 1: 15 g/ha Safener no. 2,01: 4 g/ha
Barley	30	0
Chenopodium	90	90
Emex	80	90
Raphanus	80	80
Setaria	70	70

TABLE B11

Plant:	Herbicide of formula 1: 60 g/ha	Herbicide of formula 1: 60 g/ha Safener no. 5.006: 15 g/ha
Barley	40	30
Chenopodium	90	80
Emex	90	90
Raphanus	80	70
Setaria	80	80

The same results are obtained by formulating a compound of formulae I and IIa to IIk in accordance with Examples F1, F2 and F4 to F7.

Example B3

Post-emergent Applications of Mixtures of a Herbicide of Formula I with a Safener of Formulae IIa to IIk to Durum Wheat.

Under greenhouse conditions, durum wheat is grown in plastic pots to the 2.5-leaf stage. In this stage, both the herbicide of formula I alone and the mixture of the herbicide with a safener of formulae IIa to IIk are applied to the test plants. The test substances (Formulation Examples F3 a) and b)) are applied as aqueous suspension with 500 l water/ha. Ten days after the application, the results are evaluated on a percent scale. The results obtained show that, with the safeners of formulae IIa to IIk, the damage caused to durum wheat can be markedly reduced by the herbicide of formula I. Examples of the selective effect of the compositions of the invention are given in Table B12:

TABLE B12

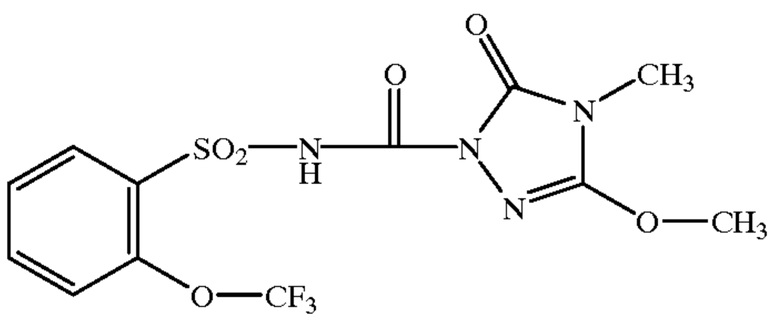
Plant:	Herbicide of formula 1: 250 g/ha	Herbicide of formula 1: 250 g/ha Safener no. 2,01: 60 g/ha
Durum wheat	30	10
Chenopodium	90	95
Emex	90	90
Raphanus	90	80
Setaria	80	80

What is claimed is:

1. A selective herbicidal composition comprising, in addition to customary inert formulation assistants, a mixture of

a) a herbicidally effective amount of a herbicide of formula I

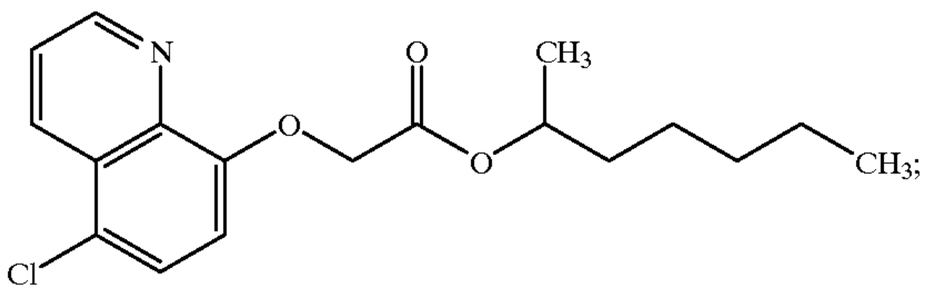
(I)



and

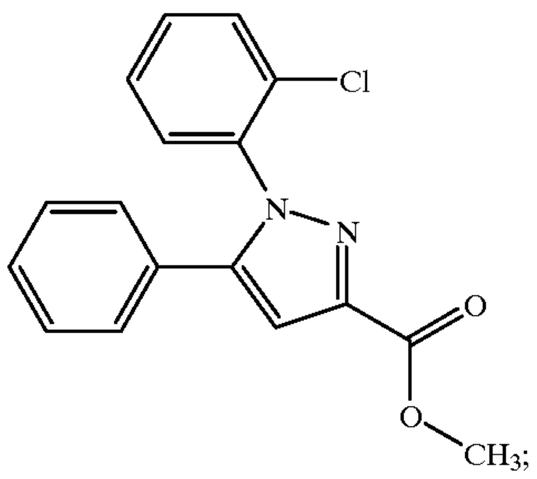
b) to antagonize the herbicide, an antidotally effective amount of a safener selected from the group of the compounds of formula 1.01

(1.01)



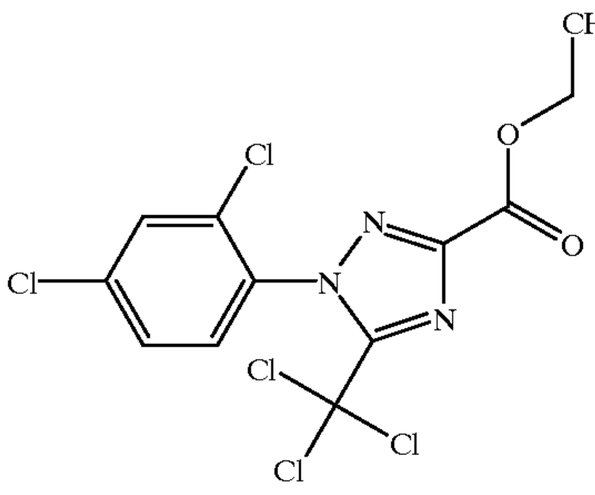
and 2.01

(2.01)



and 2.05

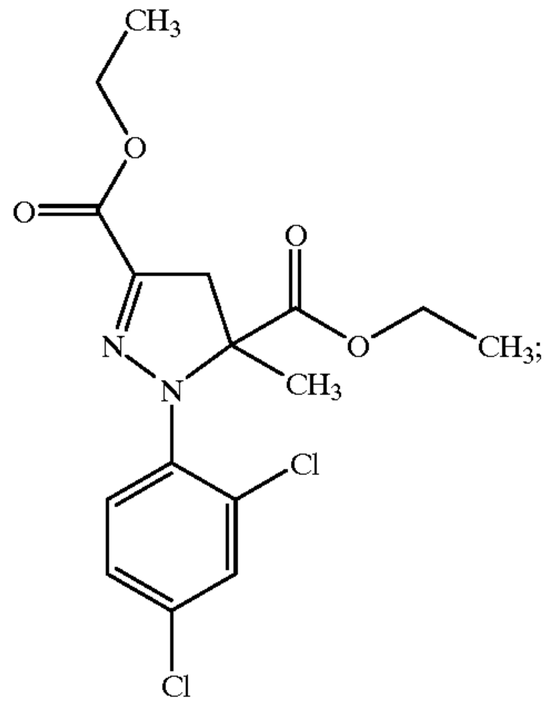
(2.05)



and 3.03

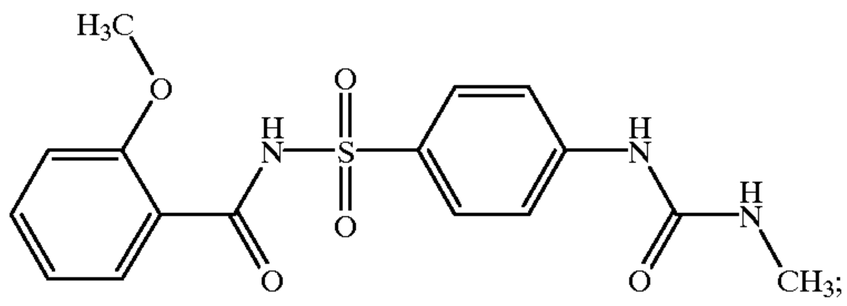
-continued

(3.03)



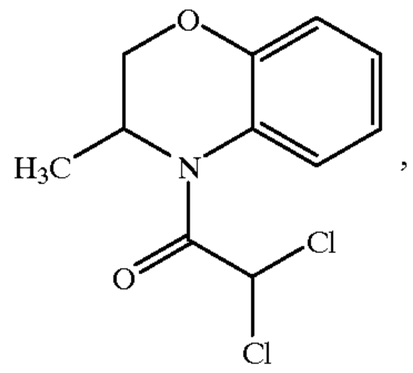
and 4.001

(4.001)



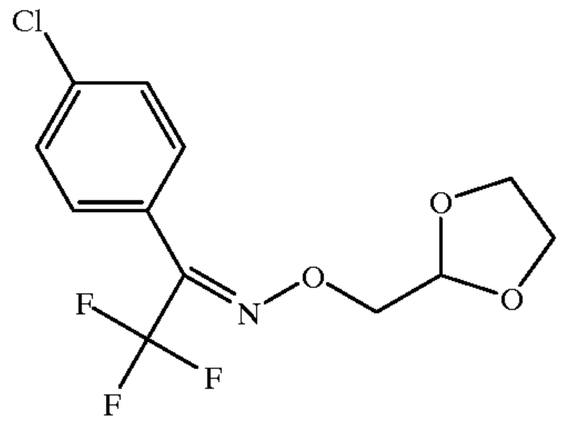
and 5.006

(5.006)



and 6.02

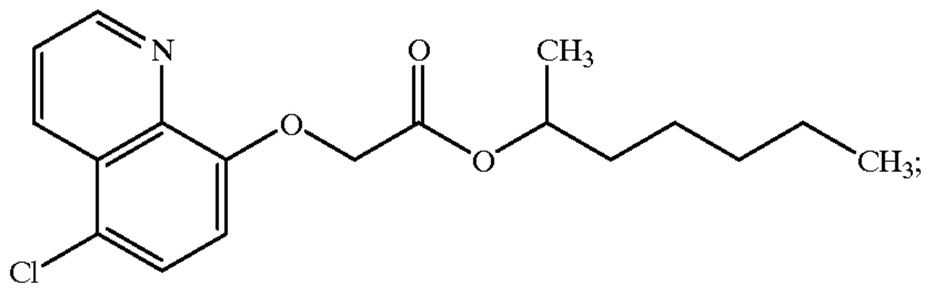
(6.02)



2. A method of selectively controlling weeds in crops of cultivated plants, which comprises treating said cultivated plants, the seeds or seedlings or the crop area thereof with a herbicidally effective amount of the compound of formula I and, to antagonise the herbicide, an antidotally effective amount of the safener selected from the group of the compounds of formula 1.01

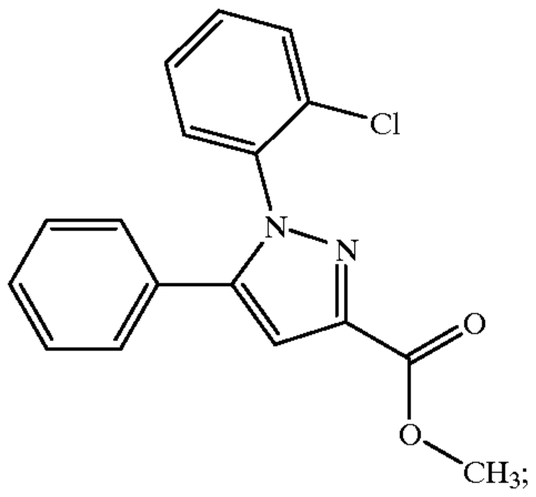
-continued

(1.01)



and 2.01

(2.01)

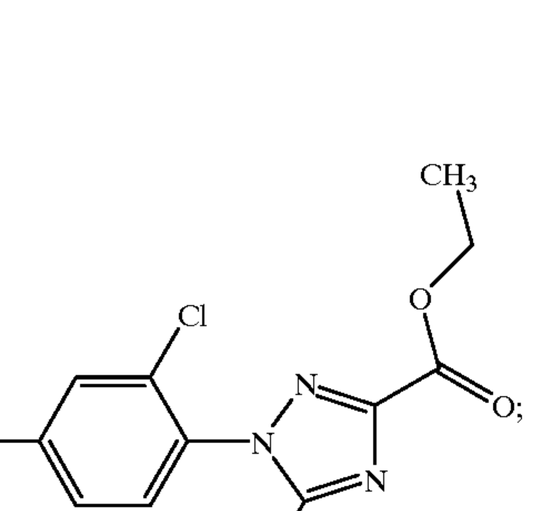


and 2.05

(2.05)

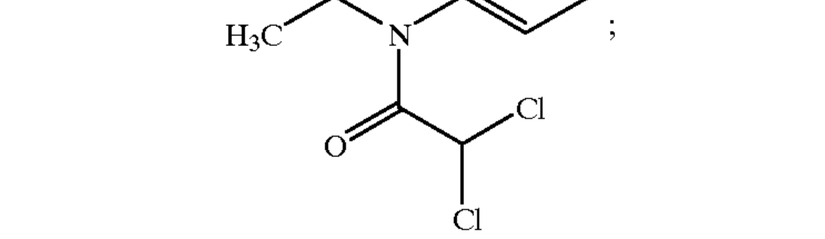
and 3.03

(3.03)



and 4.001

(4.001)

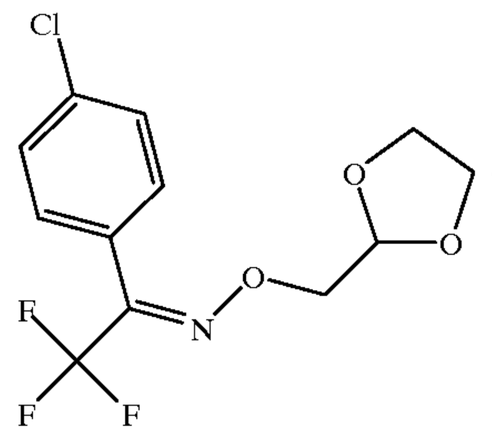


and 5.006

(5.006)

and 6.02

(6.02)



3. A method according to claim 2 wherein the cultivated plants are cereals or rice.

4. A method according to claim 2, which comprises treating crops of cultivated plants, or areas intended for cropping with cultivated plants, with 0.001 to 2 kg/ha of a herbicide of formula I and an amount of 0.001 to 0.5 kg/ha of a safener of formula II.

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